
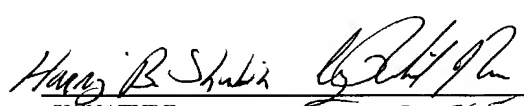


FORM PTO-1390 (REV 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371</b>				ATO CM 247	
				U.S. APPLICATION NO. (If known, see 37 CFR §1.5) <b>10/031201</b>	
INTERNATIONAL APPLICATION NO.		INTERNATIONAL FILING DATE		PRIORITY DATE CLAIMED	
PCT/FR00/01939		6 JULY 2000		15 JULY 1999	
TITLE OF INVENTION					
COMPOSITIONS BASED ON AN ETHYLENE VINYL COPOLYMER AND POLYPROPYLENE					
APPLICANT(S) FOR DO/EO/US					
BERTIN, Denis, et al.					
<b>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</b>					
1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. §371. 2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. §371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19 <sup>th</sup> month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. §371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. §371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)) a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)). <b>Items 11. to 16. below concern document(s) or information included:</b> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information:					

U.S. APPLICATION NO (if known) see 37 C.F.R. § 1.51 <b>10/031201</b>		INTERNATIONAL APPLICATION NO PCT/FR00/01939		ATTORNEY'S DOCKET NUMBER ATOCM 247	
17. <input checked="" type="checkbox"/> The following fees are submitted:  <b>BASIC NATIONAL FEE ( 37 CFR §1.492 (a) (1) - (5)):</b>  Search Report has been prepared by the EPO or JPO..... \$890.00 International preliminary examination fee paid to USPTO (37 CFR §1.482)..... \$710.00 No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2))..... \$740.00 Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO. .... \$1040.00 International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS</b> PTO USE ONLY	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. §1.492(e))					
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	29 - 20 =	9	x \$ 18.00	\$162.00	
Independent claims	1 - 3 =	0	x \$ 84.00	\$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 280.00		
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$1,052.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be					
<b>SUBTOTAL =</b>				<b>\$1,052.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. §1.492(f)).					
<b>TOTAL NATIONAL FEE =</b>				<b>\$1,052.00</b>	
Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3.31). \$40.00 per property.					
<b>TOTAL FEES ENCLOSED =</b>				<b>\$1,052.00</b>	
				Amount to be refunded:	
				charged:	
a. <input checked="" type="checkbox"/> A check in the amount of <u>\$1,052.00</u> to cover the above fees is enclosed  b. <input type="checkbox"/> Please charge my Deposit Account No. <u>13-3402</u> in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed.  c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>13-3402</u> . A duplicate copy of this sheet is enclosed.					
<b>NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO. Customer Number 23,599					
 <b>23599</b> PATENT TRADEMARK OFFICE			 SIGNATURE <u>Harry B. Shubin</u> NAME <u>32,004</u> REGISTRATION NUMBER		
Filed: 15 JANUARY 2002 HBS/kmo					

531 Rec'd PCT/PTC 15 JAN 2002

International Application No.	:	PCT/FR00/01939
International Filing Date	:	06 July 2000
Priority Date(s) Claimed	:	15 July 1999
Applicant(s) (DO/EO/US)	:	BERTIN, Denis et al.
Title: COMPOSITIONS BASED ON AN ETHYLENE-VINYL ALCOHOL COPOLYMER AND POLYPROPYLENE		

## ATOCM 247

Please replace the subtitle on page 4, line 12, with the following:

--Summary of the Invention--.

Please delete the subtitle on page 4, line 24.

# **IN THE CLAIMS**

Please amend the claims as follows:

1. (Amended) A composition comprising (by weight):
  - 55 to 99.5 parts of an EVOH copolymer,
  - 0.5 to 45 parts of polypropylene (A) and of compatibilizer (B), the proportions of (A) and (B) being such that (A)/(B) is between 1 and 5,
  - the ratio of the MFI of the EVOH to the MFI of the polypropylene being greater than 5, MFI denoting the melt flow index measured in g/10 mn at 230°C/2.16 kg.
2. (Amended) The composition as claimed in claim 1, in which the MFI of (A) is between 0.5 and 3.
3. (Amended) The composition as claimed in claim 1, in which the ratio of the MFI of the EVOH to the MFI of the polypropylene is between 5 and 25.
5. (Amended) The composition as claimed in claim 1, in which the (A)/(B) weight ratio is between 2 and 4.
6. (Amended) The composition as claimed in claim 1, in which (B) is a polyethylene grafted with polyamide grafts which results from the reaction of (i) a copolymer (B1) of ethylene and an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2).
8. (Amended) The composition as claimed in claim 1, in which (B) is a polypropylene grafted with polyamide grafts which results from the reaction of (i) a propylene

homopolymer or copolymer (B3) comprising an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2).

10. (Amended) The composition as claimed in claim 6, in which (B2) is chosen from PA-6, PA-11, PA-12, the copolyamide containing nylon-6 units and nylon-12 units (PA-6/12) and the copolyamide based on caprolactam, hexamethylenediamine and adipic acid (PA-6/6,6).

11. (Amended) The composition as claimed in claim 6, in which (B2) is a monoaminated oligomer of PA-6.

12. (Amended) A film comprising a composition according to claim 1.

13. (Amended) A film as claimed in claim 12, comprising at least one polypropylene layer.

14. (Amended) A multilayer structure comprising a film as claimed in claim 12 and packaging articles comprising these structures.

Please add the following new claims:

--15. The composition as claimed in claim 6, in which the ratio of the MFIs is between 8 and 15.

16. The composition as claimed in claim 7, in which the ratio of the MFIs is between 8 and 15.

17. The composition as claimed in claim 8, in which the ratio of the MFIs is between 8 and 15.

18. The composition as claimed in claim 9, in which the ratio of the MFIs is between 8 and 15.

19. The composition as claimed in claim 10, in which the ratio of the MFIs is between 8 and 15.

20. The composition as claimed in claim 3, in which the (A)/(B) weight ratio is between 2 and 4.

21. The composition as claimed in claim 4, in which the (A)/(B) weight ratio is between 2 and 4.

22. The composition as claimed in claim 5, in which the (A)/(B) weight ratio is between 2 and 4.

23. The composition as claimed in claim 6, in which the (A)/(B) weight ratio is between 2 and 4.

24. The composition as claimed in claim 7, in which the (A)/(B) weight ratio is between 2 and 4.

25. The composition as claimed in claim 15, in which the (A)/(B) weight ratio is between 2 and 4.

26. The composition as claimed in claim 16, in which the (A)/(B) weight ratio is between 2 and 4.

27. The composition as claimed in claim 17, in which the (A)/(B) weight ratio is between 2 and 4.

28. The composition as claimed in claim 18, in which the (A)/(B) weight ratio is between 2 and 4.

29. The composition as claimed in claim 19, in which the (A)/(B) weight ratio is between 2 and 4.--

**Cornelius**

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned “**Version With Markings to Show Changes Made**”.

*J. F. Miller*

**Filed: January 11, 2002**

- 6 -

ATOCM 247



## ABSTRACT OF THE DISCLOSURE

A composition comprising (by weight): 55 to 99.5 parts of EVOH copolymer, 0.5 to 45 parts of polypropylene (A) and a compatibilizing agent (B) e.g. a polyethylene grafted with polyamide groups, the proportions of (A) and (B) being such that (A)/(B) ranges between 1 and 5 especially between 2 and 4; the ratio of the MFI of EVOH over the MFI of polypropylene is higher than 5 especially between 5 and 25, particularly between 8 and 15, MFI representing the melt flow index. Said composition is useful for making barrier films, in particular for oxygen, used in packaging.

COMPOSITIONS BASED ON AN ETHYLENE-VINYL ALCOHOL  
COPOLYMER AND POLYPROPYLENE

[Field of the invention]

5

The present invention relates to compositions based on an ethylene-vinyl alcohol copolymer (EVOH) and polypropylene. EVOH copolymers are a barrier to many gases, and in particular to oxygen. Many articles of food packaging comprise a layer consisting of an EVOH film. Compositions based on EVOH and polyolefin and rich in EVOH also have good barrier properties. The compositions of the invention are useful for making barrier films in articles of food packaging.

15

[The technical problem]

In general, EVOH copolymers have various excellent properties such as an oxygen impermeability property, mechanical strength, etc., and find application, as they are, in many uses such as films, sheets, materials for containers, textile fibers, etc. However, this copolymer gives rise to a variation in the thickness of the product in the moulding process for manufacturing a film or a sheet, with a consequent lowering of the commercializability of the product, and, because of the shortcoming in stretchability and flexibility, gives

25

rise to non-uniform drawing during deep drawing and other processes involving a stretching force, or pin holes during the use of the product, thus imposing serious limitations on its application as a raw material for packaging. Polyolefins may be added to EVOH, the blends obtained being more flexible and being more easily converted. However, it is not known how to add more than 20% whilst maintaining the barrier properties.

10       The oxygen barrier of EVOH copolymers is greatly reduced when the relative humidity (RH) increases, whereas blends of EVOH and polyolefin are less sensitive to relative humidity - a further reason for adding polyolefins to EVOH.

15       Another reason for adding polyolefins to EVOH is that polyolefins are generally much less expensive than EVOH.

20       One objective of the present invention is to prepare EVOH-based compositions containing as much polypropylene as possible, while at the same time maintaining good barrier properties.

[Prior art]

25       Patent EP 418 129 discloses EVOH-based blends comprising 9.5 to 14.25% polypropylene and 5% compatibilizer. These blends are easily converted, the films obtained being used in packaging articles.

Patent EP 441 662 discloses the same blends but shows that the films obtained from these blends withstand hot water and steam better than pure EVOH films, that is to say the packaging articles comprising these films are resistant to sterilization. This advantage is important in the case of articles of food packaging. In both these patents, the ratio of the MFI of the EVOH to the MFI of the polypropylene is equal to 3, the MFIs being measured at 230°C under a load of 2.16 kg. The Applicant has tried to increase the proportion of polypropylene in the blend, but has not been able to convert it into film.

Patent EP 440 559 discloses blends of EVOH, polyolefin and compatibilizer. Comparative Example 4 shows a blend (by weight) of 60% EVOH, 35% polypropylene and 5% compatibilizer, that is to say the ratio of the amount of polypropylene to that of compatibilizer is equal to 7. The film obtained is not an oxygen barrier.

Patent EP 444 977 discloses blends of EVOH, polyolefin and compatibilizer. Comparative Example 4 shows a blend (by weight) of 55% EVOH, 20% polypropylene and 25% compatibilizer, that is to say the ratio of the amount of polypropylene to that of compatibilizer is equal to 0.8. The film obtained is not an oxygen barrier. In addition, in this blend the ratio of the MFI of the EVOH to the MFI of the polypropylene is equal to 0.29.

The Applicant has now discovered that, by choosing the ratio of the MFI of the EVOH to that of the polypropylene above 5 and by choosing the proportion of the compatibilizer and of the polypropylene so that the ratio of the amount of polypropylene to that of compatibilizer is between 1 and 5, blends of EVOH, polypropylene and compatibilizer possibly containing up to 45% polypropylene were obtained. In addition, these blends are easily convertible and are good oxygen barriers. Further advantages will appear below.

[Brief description of the invention]

The present invention relates to a composition comprising (by weight):

- 55 to 99.5 parts of an EVOH copolymer,
- 0.5 to 45 parts of polypropylene (A) and of compatibilizer (B), the proportions of (A) and (B) being such that (A)/(B) is between 1 and 5,
- the ratio of the MFI of the EVOH to the MFI of the polypropylene being greater than 5, "MFI" denoting the melt flow index.

[Detailed description of the invention]

The EVOH copolymer is also called a saponified ethylene-vinyl acetate copolymer. The saponified ethylene-vinyl acetate copolymer to be employed

according to the present invention is a copolymer having an ethylene content of 20 to 60 mol%, preferably 25 to 55 mol%, the degree of saponification of its vinyl acetate component not being less than 95 mol%.

5        With an ethylene content of less than 20 mol%, the oxygen impermeability property under high humidity conditions is not as high as would be desired, whereas an ethylene content exceeding 60 mol% leads to reductions in the oxygen impermeability property, in  
10    the printability and in other physical properties. When the degree of saponification or of hydrolysis is less than 95 mol%, the oxygen impermeability property and the wet strength are sacrificed. Among these saponified copolymers, those which have melt flow indices in the  
15    range of 0.5 to 100 g/10 minutes are particularly useful. Advantageously, the MFI is chosen between 10 and 30 (g/10 mm at 230°C/2.16 kg), while still satisfying the ratio with the MFI of the polypropylene.

It will be understood that this saponified  
20    copolymer may contain small proportions of other comonomer ingredients, including  $\alpha$ -olefins such as propylene, isobutene,  $\alpha$ -octene,  $\alpha$ -dodecene,  $\alpha$ -octadecene, etc., unsaturated carboxylic acids or their salts, partial alkyl esters, complete alkyl esters,  
25    nitriles, amides and anhydrides of the said acids, and unsaturated sulphonic acids or their salts.

The oxygen permeability of the EVOH copolymer films which is measured according to ASTM D 3985 is

expressed in  $\text{cm}^3$  of oxygen per  $\text{m}^2$  per 24 hours for a pressure difference of 1 bar and a thickness of 25  $\mu\text{m}$ . To simplify matters, it will be denoted in the rest of the text as  $\text{O}_2\text{GTR}$ .

5            $\text{O}_2\text{GTR}$  varies proportionally with the inverse of the film thickness.

          An EVOH comprising 38 mol% of ethylene units has an  $\text{O}_2\text{GTR}$  of 0.72 for 0% RH and 3.1 for 75% RH.

          An EVOH comprising 29 mol% of ethylene units has  
10       an  $\text{O}_2\text{GTR}$  of 0.1 for 0% RH and 1.41 for 75% RH. These grades are produced on an industrial scale and are commercially available.

          One or other of these grades is used in different thicknesses depending on the barrier required (nature  
15       of the product to be preserved, preservation time, etc.).

          With regard to (A), this is a polypropylene, homopolymer or copolymer, the copolymer possibly being of the block or random type. With regard to copolymers,  
20       the copolymer may be chosen from alpha-olefins having up to 30 carbon atoms. By way of examples of alpha-olefins, mention may be made of 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene,  
25       1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1-octacocene and 1-triacontene. These alpha-olefins may be used by themselves or as a mixture of two or more of them.

The comonomer may also be a diene. (A) may be blended with EPR (the abbreviation for Ethylene-Polypropylene-Rubber, an ethylene-propylene elastomer) or with EPDM (the abbreviation for Ethylene-Polypropylene-Diene Monomer, an ethylene-polypropylene-  
5 diene elastomer).

Advantageously, the polymer (A), which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of propylene.

10 Advantageously, the MFI of (A) is between 0.5 and 3 (in g/10 mm at 230°C/2.16 kg) and preferably 1 to 2.5, while still, of course, satisfying the condition of the MFI ratio with EVOH.

The MFIs used in the ratio of the MFI of the EVOH  
15 to the MFI of the polypropylene are measured under the same temperature conditions and under the same load. Advantageously, the measurement is carried out at 230°C under a load of 2.16 kg. According to an advantageous embodiment, this ratio is between 5 and 25 and  
20 preferably between 8 and 15. Values above 25 or even between 30 and 40 are possible, but they are of little interest because the corresponding EVOH-based compositions are not always reproducible.

As regards the compatibilizer (B), this is any  
25 polymer allowing the polypropylene to be dispersed in the EVOH. By way of example, mention may be made of functionalized polyolefins such as ethylene homopolymers or maleic-anhydride-grafted copolymers,



propylene homopolymers or maleic-anhydride-grafted copolymers and maleic-anhydride-grafted EPR or EPDM elastomers. Advantageously (B) is either a polyethylene carrying polyamide grafts or a polypropylene carrying polyamide grafts.

With regard to polyethylene carrying polyamide grafts, this results from the reaction of (i) a copolymer (B1) of ethylene and an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2). The starting point is the preparation of (B1), which is either a copolymer of ethylene and an unsaturated monomer X, or a polyethylene onto which an unsaturated monomer X is grafted. X is any unsaturated monomer that can be copolymerized with ethylene or grafted onto polyethylene and having a functional group that can react with a polyamide. This functional group may be a carboxylic acid, a dicarboxylic acid anhydride, an epoxy, etc.

By way of examples of monomer X, mention may be made of (meth)acrylic acid, maleic anhydride, unsaturated epoxides such as glycidyl (meth)acrylate, etc. Advantageously, maleic anhydride is used.

With regard to polyethylenes onto which X is grafted, polyethylene is understood to mean homopolymers or copolymers.

By way of comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms - they were mentioned above and also include polypropylene;

5       - the esters of unsaturated carboxylic acids, such as, for example, alkyl (meth)acrylates, the alkyls possibly having up to 24 carbon atoms; examples of alkyl acrylates or methacrylates are, especially, methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;

10       - vinyl esters of saturated carboxylic acids, such as, for example, vinyl acetate or vinyl propionate;

- dienes such as, for example, 1,4-hexadiene.

- the polyethylene may include several comonomers.

Advantageously, the polyethylene, which may be a  
15       blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of ethylene and its density may be between 0.86 and 0.98 g/cm<sup>3</sup>. The MFI (viscosity index at 190°C/2.16 kg) is advantageously between 1 and 1000 g/10 min.

20       By way of example of polyethylenes, mention may be made of:

- low-density polyethylene (LDPE);

- high-density polyethylene (HDPE);

- linear low-density polyethylene (LLDPE);

25       - very low-density polyethylene (VLDPE);

- polyethylene obtained by metallocene catalysis, that is to say polymers obtained by the copolymerization of ethylene and an alpha-olefin such

5

- 15

20

25

With regard to the copolymers of ethylene and monomer X, that is to say those in which X is not grafted, these are copolymers of ethylene and X and optionally another monomer, which can be chosen from the comonomers mentioned above in the case of the ethylene copolymers to be grafted by X. Advantageously, ethylene-maleic anhydride and ethylene-alkyl (meth)acrylate-maleic anhydride copolymers are used.

These copolymers comprise from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate. Their MFI is between 1 and 50 (190°C - 2.16 kg). The alkyl (meth)acrylates have already been described above.

Polyamide (B2) should be understood to mean the products of the condensation:

- of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids of one or more lactams, such as caprolactam, oenantholactam and lauryllactam;

- of one or more salts or mixtures of diamines, such as hexamethylenediamine, dodecamethylenediamine, metaxylylenediamine, bis(p-aminocyclohexyl)methane and trimethylhexamethylenediamine with diacids, such as isophthalic, terephthalic, adipic, azeleic, suberic, sebacic and dodecanedicarboxylic acids;

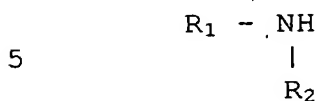
- or of mixtures of several monomers, thereby resulting in copolyamides.

Blends of polyamides may be used. Advantageously, PA-6, PA-11, PA-12, the copolyamide containing nylon-6 units and nylon-12 units (PA-6/12) and the copolyamide based on caprolactam, hexamethylenediamine and adipic acid (PA-6/6.6) may be used.

(B2) is a polyamide or a polyamide oligomer. Polyamide oligomers are described in EP 342 066.

The polyamides (B2) may have acid, amine or monoamine terminal groups. For the polyamide to have a

monoamine terminal group, all that is required is to use a chain stopper of formula:



in which:

10            $R_1$  is hydrogen or a linear or branched alkyl group containing up to 20 carbon atoms;

$R_2$  is a group having up to 20 linear or branched, alkyl or alkenyl carbon atoms, a saturated or unsaturated cycloaliphatic radical, an aromatic radical or a combination of the above. The stopper may, for  
15           example, be laurylamine or oleylamine.

          Advantageously, (B2) is a PA-6, a PA-11 or a PA-12. According to another advantageous embodiment of the invention (B2) is a monoaminated oligomer of PA-6, preferably having a mass of between 1000 and 3500.

20           The proportion of (B2) in B1 + B2 by weight is advantageously between 0.1 and 60%.

          The reaction of (B1) with (B2) preferably takes place in the molten state. (B1) and (B2) may, for example, be mixed in an extruder at a temperature  
25           generally of between 230 and 250°C. The average residence time of the melt in the extruder may be between 10 seconds and 3 minutes, and preferably between 1 and 2 minutes.

          With regard to (B), a polypropylene carrying  
30           polyamide grafts, this results from the reaction of (i)

a propylene homopolymer or copolymer (B3) comprising an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2).

The process starts with the preparation of (B3) which is either a copolymer of propylene and an unsaturated monomer X, or a polypropylene onto which an unsaturated monomer X is grafted. X is any unsaturated monomer that can be copolymerized with propylene or grafted onto polypropylene, and possessing a functional group that can react with a polyamide. This functional group was defined above. With regard to grafted polypropylenes, X may be grafted onto propylene homopolymers or copolymers, such as ethylene-propylene copolymers containing predominantly propylene (in terms of moles). Grafting is an operation known per se. With regard to (B3) in which X is grafted, X may be firstly grafted in the same extruder, in the first zones, and then the product (B2) may be introduced a few zones further downstream. (B2) was defined above.

The reaction between (B3) and (B2) takes place under the same conditions as the reaction between (B1) and (B2).

Advantageously, the ratio (by weight) of (A) to (B) is between 2 and 4.

The blends of the invention may be prepared by melt blending in extruders (single-screw or twin-screw), Buss kneaders, Brabender mixers and, in general, the usual devices for blending thermoplastics.

The compositions according to the invention may furthermore contain at least one additive chosen from:

- dyes;
- pigments;
- 5 - brighteners;
- antioxidants;
- UV stabilizers.

The invention also relates to the films consisting of the above compositions, to the multilayer structures comprising a film or a layer consisting of the above compositions and to the packaging articles comprising these structures.

According to one embodiment, the invention provides a film comprising at least one layer of a composition according to the invention and at least one adjacent polypropylene layer. The adhesion between these two layers is good. This film may especially be produced by coextrusion.

The polypropylene is a polypropylene homopolymer or copolymer. As comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 4 to 30 carbon atoms;
- dienes.

The polypropylene may also be a copolymer having polypropylene blocks.

As examples, mention may be made of:

- polypropylene homopolymer;

- polypropylene/EPDM or polypropylene EPR  
blends possibly also containing 1 to 20% polyethylene.

Advantageously, the polypropylene, which may be a  
blend of several polymers, comprises at least 50 mol%  
5 and preferably 75 mol% of propylene.

The polypropylene has, for example, an MFI of  
between 20 and 40 g/10 min (230°C/2.16 kg).

[Examples]

10

The following materials were used:

15

EVOH E ethylene-vinyl alcohol copolymer  
containing 38 mol% of ethylene, having  
an MFI of 8 (210°C/2.16 kg), a melting  
point of 183°C, a crystallization  
temperature of 160°C and a  $T_g$  (glass  
transition temperature) of 61°C;

20

EVOH D ethylene-vinyl alcohol copolymer  
containing 29 mol% of ethylene, having  
an MFI of 15 (230°C/2.16 kg), a melting  
point of 188°C, a crystallization  
temperature of 163°C and a  $T_g$  (glass  
transition temperature) of 62°C;

25

EVOH DC ethylene-vinyl alcohol copolymer  
containing 32 mol% of ethylene, having  
an MFI of 6 (230°C/2.16 kg), a melting  
point of 188°C, a crystallization



temperature of 163°C and a  $T_g$  (glass transition temperature) of 62°C;

5' PP 3020 GN 3 polypropylene supplied by Appryl®, a random copolymer having a melting point of 148°C (10°C/minute) and an MFI of 1.8 (230°C/2.16 kg);

10 PP 3010 GN 5 polypropylene supplied by Appryl®, a block copolymer having a melting point of 163°C (10°C/minute) and an MFI of 1.4 (230°C/2.16 kg);

VESTOLEN P9000® polypropylene supplied by Hüls, having an MFI of 2 (230°C/2.16 kg);

15 MOPLEN random polypropylene containing 3% ethylene and having an MFI of 2 (230°C/2.16 kg);

20 COMP 1 compatibilizer, an ethylene-polypropylene copolymer containing 88 mol% of polypropylene grafted by 1% of maleic anhydride and then condensed with a monoaminated nylon-6 oligomer of 2500 mass;

25 COMP 2 compatibilizer, an ethylene-polypropylene copolymer containing 88 mol% of polypropylene grafted by 1% of maleic anhydride.

The blends were produced on a Buss® 15D kneader.

The results are given in Table 1 below, in which the proportions are by weight.

TABLE 1

Examples (comparative examples marked #)	1 #	2 #	3 #	4 #	5	6	7	8	9
EVOH E		100							
EVOH DC			80	80					
EVOH D	100				80	80	60	60	60
PP 3020 GN3								30	
PP 3010 GN5							30		30
VESTOLEN P9000						15			
MOPLN			15	15	15				
COMP 1			5		5	5	10	10	
COMP 2				5					10
EVOH MFI/(A) MFI at 230°C/2.16 kg			3	3	7.5	37.5	10.7	8.3	10.7
O <sub>2</sub> GTR (0% RH, 23°C)	0.08	0.7	0.3	0.3	0.2	0.1	0.4	0.3	0.4
O <sub>2</sub> GTR (75% RH, 23°C)	1.1	3	1.4	1.4	1	1.2	2	2	5.4
O <sub>2</sub> GTR (75% RH)/O <sub>2</sub> GTR (0% RH) ratio	14	4	5	5	5	12	5	6	13

## CLAIMS

1. A composition comprising (by weight):
- 55 to 99.5 parts of an EVOH copolymer,
  - 5 - 0.5 to 45 parts of polypropylene (A) and of compatibilizer (B), the proportions of (A) and (B) being such that (A)/(B) is between 1 and 5,
  - the ratio of the MFI of the EVOH to the MFI of the polypropylene being greater than 5, "MFI" denoting
  - 10 the melt flow index.
2. The composition as claimed in claim 1, in which the MFI of (A) is between 0.5 and 3 (in g/10 mm at 230°C/2.16 kg).
3. The composition as claimed in claim 1 or 2,
- 15 in which the ratio of the MFI of the EVOH to the MFI of the polypropylene is between 5 and 25, the MFIs being measured at 230°C under a load of 2.16 kg.
4. The composition as claimed in claim 3, in which the ratio of the MFIs is between 8 and 15.
- 20 5. The composition as claimed in any one of the preceding claims, in which the (A)/(B) weight ratio is between 2 and 4.
6. The composition as claimed in any one of claims 1 to 5, in which (B) is a polyethylene carrying
- 25 polyamide grafts which results from the reaction of (i) a copolymer (B1) of ethylene and an unsaturated monomer

X, which is grafted or copolymerized, with (ii) a polyamide (B2).

7. The composition as claimed in claim 6, in which (B1) is chosen from ethylene-maleic anhydride copolymers and ethylene-alkyl (meth)acrylate-maleic anhydride copolymers, these copolymers comprising from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate.

8. The composition as claimed in any one of claims 1 to 5, in which (B) is a polypropylene carrying polyamide grafts which results from the reaction of (i) a propylene homopolymer or copolymer (B3) comprising an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2).

9. The composition as claimed in claim 8, in which (B3) is an ethylene-propylene copolymer containing predominantly, in terms of moles, propylene grafted by maleic anhydride.

10. The composition as claimed in any one of claims 6 to 9, in which (B2) is chosen from PA-6, PA-11, PA-12, the copolyamide containing nylon-6 units and nylon-12 units (PA-6/12) and the copolyamide based on caprolactam, hexamethylenediamine and adipic acid (PA-6/6,6).

11. The composition as claimed in any one of claims 6 to 9, in which (B2) is a monoaminated oligomer of PA-6.

12. Films consisting of compositions as claimed<sup>d</sup> in any one of the preceding claims.

13. Films as claimed in claim 12, comprising at least one polypropylene layer.

5 14. Multilayer structures comprising a film as claimed in claim 12 or 13 and packaging articles comprising these structures.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION  
EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété  
Intellectuelle  
Bureau international



(43) Date de la publication internationale  
25 janvier 2001 (25.01.2001)

PCT

(10) Numéro de publication internationale  
**WO 01/05887 A1**

(51) Classification internationale des brevets<sup>7</sup>: C08L 29/04,  
C08J 5/18, B32B 27/28 // (C08L 29/04, 23:12, 51:08)

(74) Mandataire: OHRESSER, François; Atofina, Dépt.  
Propriété Industrielle, Cours Michelet, La Défense 10,  
F-92091 Paris la Défense Cedex (FR).

(21) Numéro de la demande internationale:

PCT/FR00/01939

(22) Date de dépôt international: 6 juillet 2000 (06.07.2000)

(25) Langue de dépôt: français

(26) Langue de publication: français

(30) Données relatives à la priorité:  
99/09168 15 juillet 1999 (15.07.1999) FR

(71) Déposant (pour tous les États désignés sauf US): ATO-  
FINA [FR/FR]; 4/8, cours Michelet, F-92800 Puteaux  
(FR).

(81) États désignés (national): AE, AG, AL, AM, AT, AU, AZ,  
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE,  
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,  
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,  
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,  
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,  
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) États désignés (régional): brevet ARIPO (GH, GM, KE,  
LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), brevet eurasién  
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen  
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,  
MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM,  
GA, GN, GW, ML, MR, NE, SN, TD, TG).

Publiée:

— Avec rapport de recherche internationale.

En ce qui concerne les codes à deux lettres et autres abrévia-  
tions, se référer aux "Notes explicatives relatives aux codes et  
abréviations" figurant au début de chaque numéro ordinaire de  
la Gazette du PCT.

(54) Title: COMPOSITIONS BASED ON AN ETHYLENE VINYL COPOLYMER AND POLYPROPYLENE

(54) Titre: COMPOSITIONS A BASE D'UN COPOLYMERE DE L'ETHYLENE ET DE L'ALCOOL VINYLIQUE ET DE PO-  
LYPROPYLENE

(57) Abstract: The invention concerns a composition comprising (by weight): 55 to 99.5 parts of EVOH copolymer; 0.5 to 45  
parts of polypropylene (A) and compatibilising agent (B), the proportions of (A) and (B) being such that (A)/(B) ranges between 1  
and 5; the ratio of the MFI of EVOH over the MFI of polypropylene is higher than 5, MFI representing the melt flow index. Said  
composition is useful for making barrier films, in particular for oxygen, used in packaging.

(57) Abrégé: La présente invention concerne une composition comprenant (en poids): 55 à 99,5 parties de copolymère EVOH, 0,5  
à 45 parties de polypropylène (A) et de compatibilisant (B), les proportions de (A) et (B) étant telles que (A)/(B) est compris entre  
1 et 5, le rapport du MFI de l'EVOH au MFI du polypropylène est plus grand que 5, "MFI" désignant l'indice de fluidité à l'état  
fondu. Cette composition est utile pour faire des films barrière en particulier à l'oxygène qu'on utilise dans l'emballage.

WO 01/05887 A1

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); John H. Thomas (33,460); Catherine M. Joyce (40,668); Nancy J. Axelrod (44,014); James T. Moore (35,619); James E. Ruland (37,432); Jennifer J. Branigan (40,921) and Robert E. McCarthy (46,044).

Send Correspondence to Customer Number 23599



23599

PATENT TRADEMARK OFFICE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of sole or first inventor (given name, family name)

Denis BERTIN

Signature

Denis Bertin

Date

03/19/2002

Residence

Plan de Cuques, France FRX

Citizenship

France

Post Office Address

Residence la Bastide Madeleine, Appt. 26, 126, avenue de la Liberation, F-13380 Plan de Cuques, France

Full Name of additional joint inventor (given name, family name)

Yves GERMAIN

Signature

Yves Germain

Date

03/02/2002

Residence

Serguigny, France FRX

Citizenship

France

Post Office Address

3, allée Parc Maubuisson, F-27470 Serguigny, France

Full Name of additional joint inventor (given name, family name)

Signature

Date

Residence

Citizenship

Post Office Address

Full Name of additional joint inventor (given name, family name)

Signature

Date

Residence

Citizenship

Post Office Address

Full Name of additional joint inventor (given name, family name)

Signature

Date

Residence

Citizenship

Post Office Address

☐ Additional joint inventors are named on separately numbered sheets attached hereto.